

International Standard



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**Water quality — Determination of total mercury by
flameless atomic absorption spectrometry —
Part 1 : Method after digestion with
permanganate-peroxodisulfate**

mineralization

Qualité de l'eau — Dosage du mercure total par spectrométrie d'absorption atomique sans flamme — Partie 1 : Méthode après minéralisation au permanganate-peroxodisulfate

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been authorized has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5666/1 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in December 1981.

It has been approved by the member bodies of the following countries:

Australia	France	Poland
Austria	Germany, F.R.	Romania
Belgium	Hungary	South Africa, Rep. of
Brazil	India	Spain
Canada	Italy	Sweden
Chile	Japan	Switzerland
China	Mexico	United Kingdom
Czechoslovakia	Netherlands	USSR
Egypt, Arab Rep. of	New Zealand	
Finland	Norway	

No member body expressed disapproval of the document.

Water quality — Determination of total mercury by flameless atomic absorption spectrometry — Part 1 : Method after digestion with permanganate-peroxodisulfate

0 Introduction

This document constitutes the first part of an International Standard specifying methods for the determination of total mercury in water by flameless atomic absorption spectrometry.

Since various types of water may be tested for the presence of mercury, it has been considered preferable to standardize several methods of determination, which, although they are all based on the same instrumental technique (atomic absorption spectrometry), involve, nevertheless, sufficiently important procedural differences so that their respective fields of application differ significantly.

Thus, this part (part 1) specifies a method of determination after digestion with permanganate-peroxodisulfate and is applicable, in particular, to surface waters and domestic and industrial wastewaters.

Part 2 specifies a method of determination after mineralization by means of ultraviolet radiation and is applicable to drinking water and to candidate drinking water.

Part 3, at present under study, will specify a method of determination after digestion with bromine and will apply to soft water and brines to drinking water and to other types of water containing only small amounts of organic matter.

Each of the three parts describes the method in its entirety and can therefore be used independently of the others.

1 Scope and field of application

This part of ISO 5666 specifies a flameless atomic absorption spectrometric method for the determination of total mercury in water, and, in particular, in surface waters and in domestic and industrial wastewaters.

The method permits determination of as little as 0,05 µg of mercury in the test portion used for the analysis under the optimum instrumental conditions (minimum baseline noise of the apparatus, high spectral purity lamp, and reagents with very low mercury contents). For example if using a test portion of 100 ml, the lower limit of determination is 0,5 µg/l.

The method is not applicable if the concentration of organic matter is such that the quantity of potassium permanganate

specified in 7.3.1 is insufficient to produce a persistent intense violet coloration.

In addition, in the presence of iodide ions, the precision of the method may be perceptibly reduced (see clause 9).

2 Reference

ISO 5725, *Precision of test methods — Determination of repeatability and reproducibility by inter-laboratory tests.*

3 Principle

Digestion of a test portion, using potassium permanganate and potassium peroxodisulfate at 95 °C, in order to convert all the mercury present to mercury(II).

Reduction of the excess of oxidant with hydroxylammonium chloride and reduction of mercury(II) to metallic mercury by tin(II) chloride.

Entrainment of the mercury in a current of gas at ambient temperature and determination of the mercury, as the monatomic vapour, by flameless atomic absorption spectrometry at a wavelength of 253,7 nm.

4 Reagents

During the analysis, use only the water (4.1) and reagents of recognized analytical grade, the mercury contents of which are as low as possible¹⁾.

4.1 Demineralized-distilled water, or water of equivalent purity, free from mercury.

4.2 Sulfuric acid, $\rho_{20} = 1,84$ g/ml.

4.2.1 Sulfuric acid (4.2) diluted 1 + 1.

CAUTION — Add the acid to the water slowly and with constant stirring to avoid spattering of concentrated acid.

4.3 Nitric acid, $\rho_{20} = 1,42$ g/ml.

1) If the reagents used lead to high results in blank tests, it is necessary to use products of better quality.

4.4 Hydrochloric acid, $\rho_{20} = 1,19$ g/ml.

4.5 Hydrochloric acid, approximately 0,3 mol/l solution.

Dilute 10 ml of the hydrochloric acid (4.4) to 1 litre with water.

4.6 Potassium permanganate, 50 g/l solution.

Dissolve 50 g of potassium permanganate in water and dilute to 1 litre.

Prepare and handle this solution with care in order to avoid undissolved particles remaining or being trapped in suspension.

Store the solution in a brown glass bottle with a glass stopper.

4.7 Potassium peroxodisulfate, 50 g/l solution.

Dissolve 5 g of potassium peroxodisulphate ($K_2S_2O_8$) in 100 ml of water.

Prepare this solution daily.

4.8 Hydroxylammonium chloride, 100 g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH \cdot HCl$) in water and dilute to 100 ml.

4.9 Tin(II) chloride, solution containing 100 g of $SnCl_2 \cdot 2H_2O$ per litre.

Prepare this solution on the day of use by one of the following two methods:

a) Dissolve 25 g of tin(II) chloride dihydrate in 50 ml of warm hydrochloric acid (4.4). If cloudy, filter and add a small granule of tin to the filtrate. Cool and transfer quantitatively to a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix.

b) Dissolve, by heating in a boiling water bath, 13 g of tin in 50 ml of the hydrochloric acid (4.4). Cool, transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

Eliminate any mercury which may be present in this solution by bubbling nitrogen through it (for example during 30 min).

4.10 Potassium dichromate, 4 g/l acidic solution.

Dissolve 4 g of potassium dichromate ($K_2Cr_2O_7$) in 500 ml of water and carefully add either 500 ml of sulfuric acid ($\rho_{20} = 1,84$ g/ml) or 500 ml of the nitric acid (4.3).

4.11 Iodine, 2,5 g/l solution in 30 g/l potassium iodide solution, for absorption of mercury vapour.

4.12 Mercury, standard solution corresponding to 1 g of Hg per litre.

Weigh, to the nearest 0,001 g, 1,354 g of mercury(II) chloride ($HgCl_2$), transfer to a 1 000 ml one-mark volumetric flask and

dissolve in about 25 ml of the hydrochloric acid (4.4). Dilute to the mark with water and mix.

This solution can be stored in borosilicate glass bottles for about 1 month.

1 ml of this standard solution contains 1 mg of Hg.

NOTE — This solution can be stabilized by adding 50 ml of the acidic potassium dichromate solution (4.10) before diluting to the mark.

4.13 Mercury, standard solution corresponding to 10 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.12) to 1 000 ml with the hydrochloric acid solution (4.5).

1 ml of this standard solution contains 10 μ g of Hg.

Prepare this solution on the day of use.

4.14 Mercury, standard solution corresponding to 0,1 mg of Hg per litre.

Dilute 10,0 ml of the standard mercury solution (4.13) to 1 000 ml with the hydrochloric acid solution (4.5).

1 ml of this standard solution contains 0,1 μ g of Hg.

Prepare this solution on the day of use.

4.15 Compressed air or inert gas, in a steel cylinder.

5 Apparatus

Before use, all glassware shall be washed very carefully with the acidic potassium dichromate solution (4.10), and then rinsed several times with water (4.1).

Never dry the glassware between two operations and keep the aeration flask (5.3) full of water (4.1).

Glassware that is to be used for the first time should be treated beforehand by the following process:

- wash with concentrated nitric acid;
- wash with a mixture, prepared in the container at the moment of use, of 4 volumes of the sulfuric acid (4.2) and 1 volume of the potassium permanganate solution (4.6);
- wash with the hydroxylammonium chloride solution (4.8) to remove all deposits of manganese dioxide;
- finally, wash several times with water (4.1).

Usual laboratory equipment and

5.1 Atomic absorption spectrometer, provided with a low pressure mercury lamp (or a hollow-cathode mercury lamp), or a mercury vapour analyser.

5.2 Recorder, with a maximum signal indicator, or a peak-area integrator (see the note to 5.7).

5.3 Aeration flasks, tall form, of volume appropriate to the size of the test portion and compatible with the rest of the apparatus, bearing a calibration mark corresponding to the optimum filling level, the dead volume of which has been reduced to a minimum and through which the gas flows under the optimum conditions. For this, the aeration tube should be designed either with a finely drawn out point, a sphere pierced with holes, or a fritted end (pores of 100 to 250 μm). It is necessary to confirm that the different flasks used all lead to the same result.

After each use, treat the aeration flasks with the acidic potassium dichromate solution (4.10) to oxidize any traces of tin(II) that they may contain.

5.4 Measuring cell, with windows of quartz or of other material transparent to ultraviolet radiation (about 253,7 nm), the length of which is appropriate to the spectrometer being used.

5.5 Equipment to avoid, if necessary, any condensation of water vapour in the measuring cell. Any appropriate system may be used for this purpose (infra-red lamp, black electrical heating element, rod heater, desiccant trap, etc.).

5.6 Equipment for absorption of mercury vapour as it leaves the measuring cell (see the figure for an example).

5.7 Auxiliary equipment.

An example of the manner in which the various components are assembled is shown in the figure, together with the principle on which the apparatus works, for the case of a measuring system using an open circuit (see the note).

Any other satisfactory arrangement may be used. The entrainment gas may, for example, be air, nitrogen or argon, and an absorbing solution other than that specified may be used in the equipment J (5.6).

NOTE — It is possible to use a closed-circuit aeration system, in which the mercury vapour is recycled by means of a pump. In this case, a recorder is no longer necessary and it is possible to use a direct reading instrument or a maximum signal indicator.

6 Samples

Immediately after collection, adjust the pH of each sample to 1 or less by adding the nitric acid (4.3) (see note 1).

If the determination cannot be carried out immediately after sampling, in addition to the nitric acid, add 4 ml of the potassium permanganate solution (4.6) per litre of sample, and, if necessary, further quantities until a persistent pink coloration is obtained (see note 2). Store the samples in borosilicate glass bottles.

NOTES

1 If it is desired to measure dissolved and suspended mercury separately, carry out an appropriate separation (filtration through 0,45 μm mesh or centrifuging) of the sample immediately after collection, then add the nitric acid and the potassium permanganate solution to the liquid portion. If filtration is used for separation, use glass fibre filter in order to reduce the possible loss by adsorption.

2 Record the volume of the sample and also the volumes of reagents added, so that allowance can be made for these in the blank test and in the calculation of results. Take care to use the same reagents for both the sample and in the blank test.

7 Procedure

7.1 Test portion

Treat the entire sample (clause 6) with the hydroxylammonium chloride solution (4.8) to completely dissolve all manganese dioxide, and then, without delay, take two test portions of 100 ml each, taking care to obtain representative quantities of both dissolved and suspended portions of the sample, and immediately carry out the determination as described in 7.3. Use the second test portion for the control test (7.5).

NOTE — The volume of the test portions may be reduced if the sample contains high concentrations of mercury or organic matter.

7.2 Calibration

Prepare, at the moment of use, using the standard mercury solutions (4.13 and 4.14), at least five calibration solutions covering the range of concentrations which can be measured with the apparatus to be used (depending on the circumstances, this range may cover a part or the whole of the range 0,1 to 10 μg of mercury per litre).

Treat each of these solutions immediately after their preparation in exactly the same way as the test portion on which the determination is to be carried out (see 7.3.1 and 7.3.2).

Also proceed in exactly the same way, replacing the test portion with the water (4.1) (zero term).

As appropriate, measure either the peak heights in centimetres or the peak areas in square centimetres and plot a calibration graph.

7.3 Determination

7.3.1 Digestion

Place the test portions (7.1) or measured aliquot portions diluted to 100 ml, containing no more than 1 μg of mercury, in conical flasks with ground glass stoppers. Carefully add 10 ml of the sulfuric acid (4.2) and 2,5 ml of the nitric acid (4.3). Mix after each addition.

Add 15 ml of the potassium permanganate solution (4.6). If the intense violet coloration does not persist for at least 15 min, mix and add a further 15 ml of the potassium permanganate solution (4.6) in order to obtain a persistent coloration. Then add 8 ml of the potassium peroxodisulfate solution (4.7) and heat for 2 h in a water bath controlled at 95 °C; allow to cool to room temperature.

Keep the second test portion for the control test (7.5) and continue the determination on the first test portion.

Reduce the excess of oxidant by adding the hydroxylammonium chloride solution (4.8) until the solution is just decolorized and all oxides of manganese have dissolved. Transfer the solution to one of the aeration flasks (5.3) and add, if necessary, distilled water in order to adjust the volume to correspond to the calibration mark on the flask.

NOTE — If the 30 ml of the potassium permanganate solution is not sufficient to give a persistent coloration, either the volume of the test portion should be reduced or another method of digestion should be considered, and, in this case, this method is no longer applicable.

7.3.2 Entrainment and determination

Adjust the controls of the apparatus and the gas flow (1 l/min for example), using an aeration flask (5.3) filled with water (4.1) to the calibration mark. Wait until the apparatus and the gas flow stabilize.

Divert the gas flow and replace the aeration flask containing water by one containing the test solution (7.3.1) to which 2 ml of the tin(II) chloride solution (4.9) has just been added (see note 1). Mix, wait 30 s, and then restore the gas flow through the aeration flask. The entrainment of the mercury vapour through the measuring cell (5.4) produces a recorder tracing which rapidly attains a maximum.

If peak heights are being used as a measure of response, purge the gas circuit and replace the aeration flask with that containing water as soon as the recorder tracing begins to decrease. If peak areas are being used do not interrupt recording until the signal has returned to its initial value.

After each test, purge the aeration flask as indicated in 5.3.

NOTES

- The addition of the tin(II) chloride solution may advantageously be made after the flask has been placed in position, providing that the flask is suitably designed to allow this to be done.
- If the peak obtained during a determination does not have the same shape as that obtained from a standard solution, it is recommended that peak areas be measured and not peak heights. In all cases, the absence of interferences should be verified by means of the control test (7.5).

7.4 Blank test

Carry out a blank test, proceeding as specified in 7.3.1 and 7.3.2, but replacing the test portion by water (4.1), and using the same volumes of reagents as for the determination proper. Make allowance for the volumes of reagent added during collection of the samples (see note 2 to clause 6).

Determine the blank value for each batch of samples (see the annex).

7.5 Control test

An indication of possible interferences can be obtained by repeating the operations specified in the last paragraphs of 7.3.1 and in 7.3.2, using the second test portion reserved in 7.3.1, with the addition of a known volume of the standard mercury solution (4.13). If the mercury concentration is too high, use an aliquot portion of the test portion.

8 Expression of results

From the height or area of the peak obtained (in centimetres or in square centimetres as appropriate), in the determination, determine, by reference to the calibration graph and making allowance for the blank test, the mercury content of the test portion.

In the case of an apparatus with digital read out, or a maximum response indicator, prepare a graph of the mass of mercury against the corresponding instrument read out.

From this value, compute the total mercury content of the sample, allowing for the volumes of reagents introduced during sampling and the treatment (7.1) of the sample. Express this content in micrograms per litre.

9 Precision

A joint ISO and BITC (Bureau international technique du chlore) interlaboratory test was carried out, in November 1977, on a first sample (A) containing 0,58 µg of mercury per litre, and on a second sample (B) containing 0,67 µg of mercury per litre and 1,5 mg of iodide ions per litre.

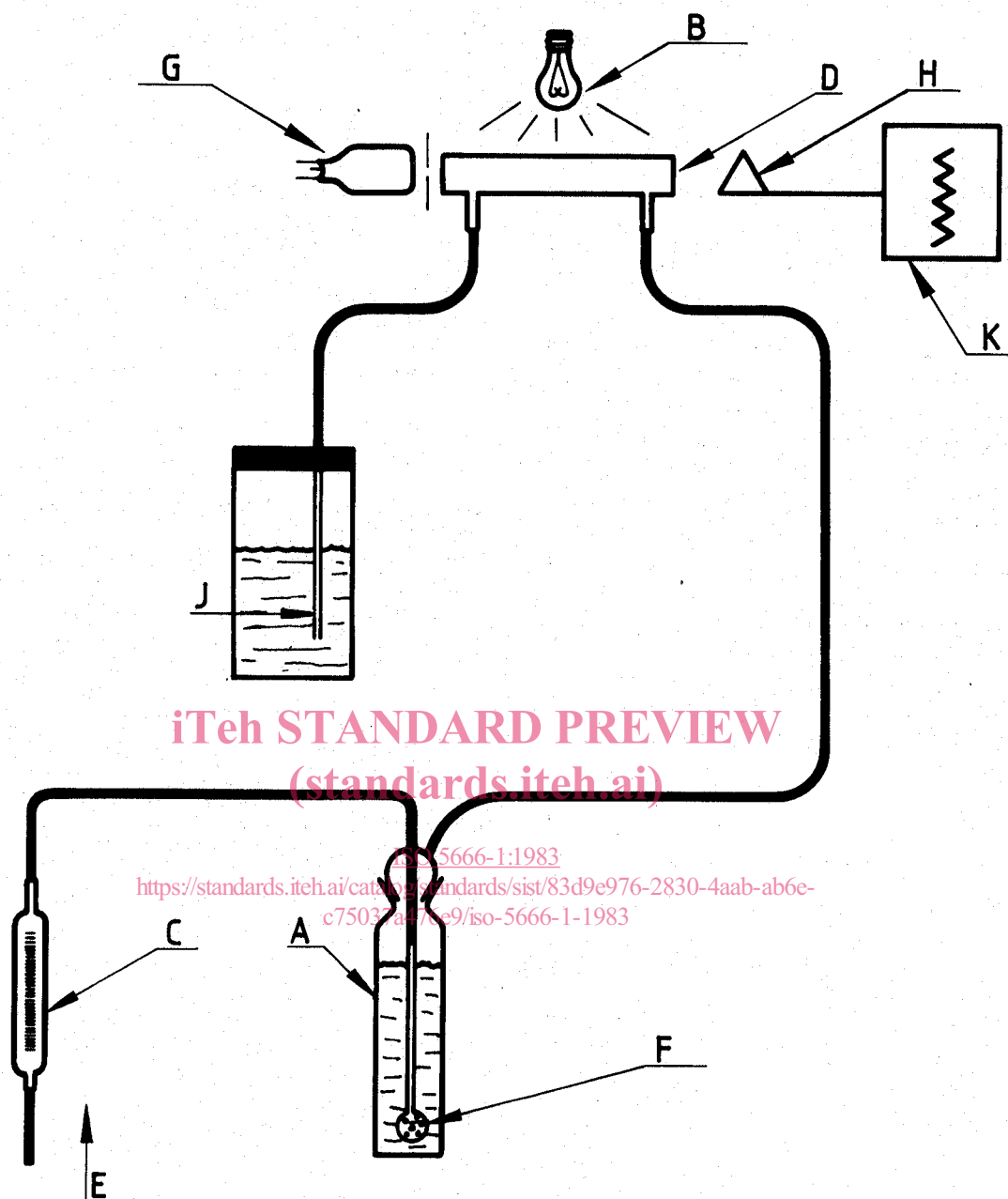
Statistical analysis of the results in accordance with ISO 5725 has given the information shown below.

10 Test report

The test report shall include the following information :

- all information necessary for complete identification of the sample;
- the method used;
- the results obtained;
- the conditions of test;
- details of any operations not included in this International Standard, or regarded as optional, together with any incidents likely to have had an influence upon the results.

Sample	Number of participating laboratories	Number of eliminated laboratories	Mean µg/l	Standard deviation			
				Repeatability		Reproducibility	
				Absolute	Relative	Absolute	Relative
A	47	3	0,580 3	0,050	8,6 %	0,166	28,6 %
B	47	5	0,560 9	0,057	10,2 %	0,326	58,0 %



- A — Aeration flask (5.3)
- B — Cell heating device (5.5)
- C — Rotameter, about 1 litre of air per minute
- D — Quartz measuring cell
- E — Compressed air or inert gas (4.15), 1 l/min
- F — Glass aeration tube with a sphere pierced with holes at the end (see 5.3)
- G — Hollow-cathode mercury lamp, or other appropriate lamp (see 5.1)
- H — Spectrometer (5.1) detection system (photomultiplier and monochromator)
- J — Equipment for absorption of mercury vapour (5.6) containing the iodide solution (4.11)
- K — Recorder (5.2)

Figure — Example of apparatus for open circuit measurement

Annex

Control of blank values

A.1 General

When carrying out determinations at concentrations close to the lower limit of detection, it is essential to control the blank values in order to ensure that the results obtained are meaningful; a realistic value for the limit of detection can, then, be established by each laboratory according to the results obtained in their own blank tests.

A.2 Evaluation and control of blank values

Several techniques, based on a statistical approach, can be applied for checking the blank values.

The following technique is given as an indication.

For the method of analysis being used, carry out a series of 10 blank tests following the appropriate procedure (7.4).

Compute the standard deviation and use the value obtained to compute the confidence interval (CI) from the expression

$$CI = \bar{x} \pm s \frac{t_{(P, f)}}{\sqrt{n}}$$

where

\bar{x} is the mean of the blank values;

s is the standard deviation;

t is Student's coefficient (2,26 in this case);

P is the bilateral confidence level chosen (95 % in this case);

f is the number of degrees of freedom (9 in this case);

n is the number of measurements (10 in this case).

Carry out a blank test daily. The result should be within the confidence interval CI. If it is significantly greater than $\bar{x} + st(n-1/2)$, check the reagents used and replace those that have mercury contents that are too high. If the blank value still exceeds the upper limit, or if it is significantly less than $\bar{x} - st(n-1/2)$, redetermine the confidence interval and deduct the limit of detection.

As an indication, the average value and the confidence interval CI (at a confidence level of 95 %) of the blanks obtained in the joint ISO and BITC (Bureau international technique du chlore) interlaboratory trial from November 1977 in which 45 laboratories participated is

CI = 0,025 ± 0,006 µg mercury (for a blank test of 100 ml)